



Solvent size effect on the static and dynamic properties of polymer chains in athermal solvents

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ABSTRACT

The static and dynamic properties of polymer chains in athermal solvents with different sizes are studied by molecular dynamics method. With increasing solvent size, the radius of gyration and the diffusion coefficient of the polymer decay fast until a critical solvent size is reached. For the polymer diffusion coefficients, this decay only depends on the solvent size; while for the radius of gyration of polymers, this decay depends on both solvent size and the length of the polymers. The increase of solvent size also makes the polymer tend to be thicker ellipsoid until a critical solvent size is reached. The static scaling exponent of the polymer also shows the solvent size dependence. Moreover, four regions are identified where the polymers show different dynamic behaviors according to the dynamic structure factors of the polymer.

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1. Introduction

Properties of polymers are strongly affected by the solubility, composition and molecular size of the solvent [1] for polymer solutions. In recent two decades, solvent size effect had attracted great attention in both theory [2,3] and experiment [4–9]. Xue and coworkers [10] had studied the depletion behavior of a polymer solution near an interface, and elucidated that the solvent with larger molecular volume intensifies the depletion effect. Senapati and Chandra [11] showed the solvent size dependence of the interfacial structure of a solute–solvent mixture in contact with a semipermeable membrane. Besides, many properties of polymers, such as phase separation [12,13], transfer free energies [14,15], polymer collapse [13,16–18], and solvent self-diffusion [19,20], have been shown affected by the solvent size. The aforementioned works explored the solvent size effect via changing the diameters of solvent particles. Recently, Li et al. [21,22] investigated solvent size effect on the gelation behavior through changing the degree of polymerization of solvent molecules and found that the physical gelation of triblock copolymers follows three kinds of mechanisms when the solvent size changes.

Here we focus on the chain-like solvent, whose size is purely controlled by changing the degree of polymerization of the solvent

molecules. With increasing solvent size, solvent changes from normal-size solvent (i.e. Single molecular solvents) to middle-size solvent and then large-size solvents, which will lead to great changes in the properties of solute polymer. In this work, the static and dynamic properties of polymer chains in athermal solvents with varying solvent sizes are investigated using molecular dynamics (MD) method, which manifests the contribution of entropy in the solvent size effect. Model and simulation details are given in Section 2, and the results and discussion are presented in Section 3. Finally, we summarize our results in Section 4.

2. Model and simulation details

We simulate one or more bead-spring polymer chains in athermal solvent with varying solvent sizes by MD method, where the solvent molecules with solvent size $N_s > 1$ are also modeled with bead-spring chain. Since there is no constrain of bond angle and chain rigidity, both solute polymer and solvent molecular will show more flexible than real polymer and solvent, and they will contribute more conformation entropy. The truncated Lennard–Jones [23] U_{LJ} and the finitely extensible nonlinear elastic (FENE) potential [24] U_{FENE} are employed to embody the excluded volume effect and the connection between neighboring monomers of the same chain, respectively.

$$U_{LJ}(r) = \begin{cases} 4\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 + \frac{1}{4} \right] & r < r_c \\ 0 & r \geq r_c \end{cases} \quad (1)$$

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and

$$U_{\text{FENE}}(r) = -\frac{k}{2}R_0^2 \ln\left(1 - \frac{r^2}{R_0^2}\right) \quad (2)$$

Here r is the distance between two beads. m is the mass of each beads. σ defines the length scale, and ε governs the strength of the interaction. Note that the reduced units are used in the simulations, where σ , ε , and m are set to be unity and $\tau_{\text{LJ}} = (m\sigma^2/\varepsilon)^{1/2}$ is the unit of time (1 time step = 0.006 τ_{LJ}). Subsequently, the cutoff diameter is set to be $r_c = 2^{1/6}$, the ultimate bond length $R_0 = 2.0$, and the spring constant $k = 7.0$ in reduced units [25].

We choose simple cubic simulation box with side length $L = 22.05$ in which the total number of particles is $N_{\text{tot}} = 9261$, i.e., the particle number density is $\rho = 0.864$ [25,26], and employ periodic boundary condition. The simulations are conducted in the canonical ensemble, where the temperature $k_B T = 1.2$ (k_B is Boltzmann constant) is controlled by Berendsen thermostat [23]. Leapfrog algorithm [23] is employed to integrate the equations of motion, and Verlet-cell list method is introduced for better computation efficiency. After 6.0×10^6 time steps relaxation, the system reaches equilibrium. Then we start to record the interesting properties of the polymers every 200 time steps in the following 6.0×10^6 time steps. Five parallel samples are run for better statistics. The validity of the program used here has been testified in the study of linear chains in Ref. [25].

In this work, the effect of solvent size on the static and dynamic properties of the polymer is studied via changing the polymerization degree N_s of the solvent chains. Several interesting properties of the polymer are listed as follows. The molecular size of the polymer explored in this work is represented by the mean square radius of gyration (R_g^2) [26], which is defined as

$$\langle R_g^2 \rangle = \frac{1}{2N^2} \sum_{m=1}^N \sum_{n=1}^N (\vec{r}_n - \vec{r}_m)^2 \quad (3)$$

where \vec{r}_n and \vec{r}_m are the position vectors of the n -th and m -th monomers. The diffusion coefficient of the mass center D_{cm} of the polymer chain is calculated via [25,26]

$$6D_{\text{cm}}t = \langle (\vec{r}_{\text{cm}}(t) - \vec{r}_{\text{cm}}(0))^2 \rangle \quad (4)$$

in which $\vec{r}_{\text{cm}}(t)$ is the position vector of the mass center of polymer chain at time t . The dynamic structure factor $S(k, t)$ of the polymer is calculated via

$$\begin{aligned} S(k, t) &= N^{-1} \sum_{ij} \langle \exp\{i\vec{k} \cdot [\vec{r}_i(t) - \vec{r}_j(0)]\} \rangle \\ &= N^{-1} \sum_{ij} \frac{\sin(k|r_i(t) - r_j(0)|)}{k|r_i(t) - r_j(0)|} \end{aligned} \quad (5)$$

where $\vec{r}_i(t)$ is the position vector of the i -th monomer at time t , $\vec{r}_j(0)$ is the position vector of the j -th monomer at time 0, and \vec{k} is wave number.

Meanwhile, the pair distribution function $G(r)$ of the polymer and the solvent chain is calculated, since it can provide insight into the solution structure and give the probability of finding a pair of atoms at distance r apart [23]. If there are $n(r)$ particles between r and $r + \Delta r$ from a given particle, we have [27]

$$G(r) = \frac{V}{N_{\text{tot}}} \left[\frac{n(r)}{4\pi r^2 \Delta r} \right], \quad (6)$$

here V and N_{tot} are the total volume and total number of particles of the simulation box, respectively.

3. Results and discussion

The critical degree of polymerization of entanglement in chain-like solvents is examined firstly, and we find no entanglement occurred when the solvent chain length is less than 120. In this work, in order to avoid the entanglement effect on the properties of the polymer solute, the degree of polymerization of the chain-like solvent and the polymer itself is no more than 100.

3.1. The properties of a single polymer chain in solvent with various solvent sizes

To clearly manifest the solvent size effect on the static and dynamic properties of polymers in athermal solvents, we firstly

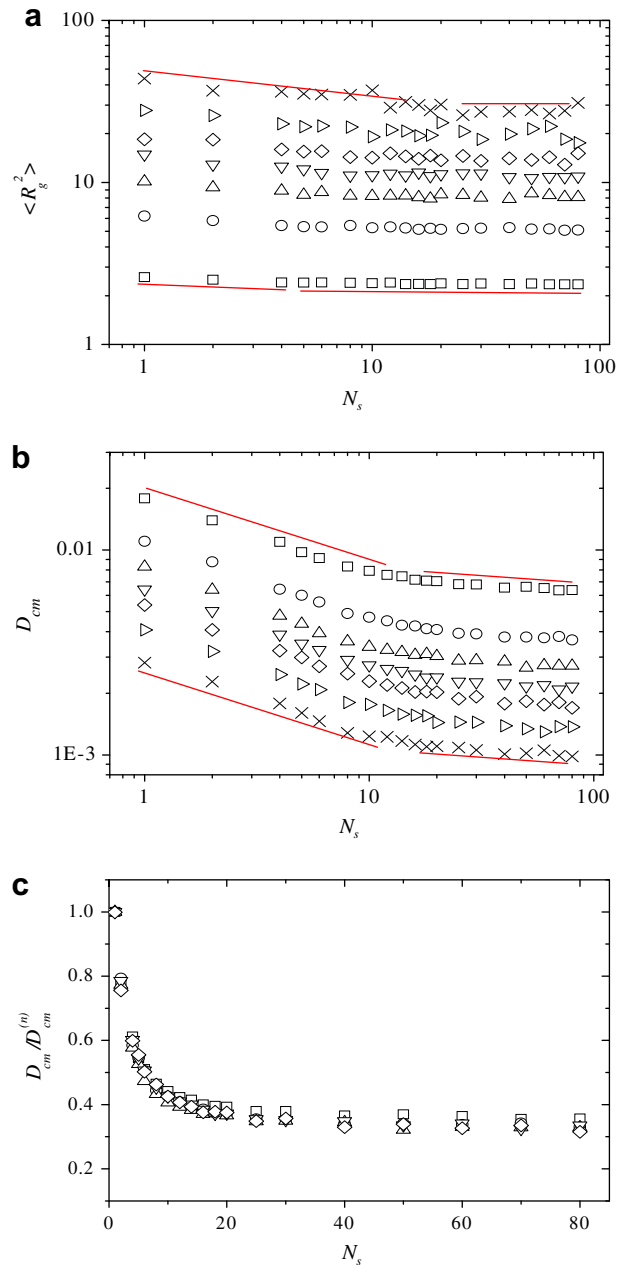


Fig. 1. (color online) The solvent size dependence of mean square radius of gyration (a), diffusion coefficient (b), and the normalized diffusion coefficient (c) of single solute polymer with $N = 10$ (\square), 20 (\circ), 30 (\triangle), 40 (∇), 50 (\diamond), 70 (\triangleright), 100 (\times). The corresponding lines are drawn for visual guide.

Table 1

The semiquantitative critical solvent size N_s^* for molecular sizes and diffusion coefficients of single solute polymers.

N	10	20	30	40	50	60	70	80	90	100
$N_s^*(R_g^2)$	4	5	7	8	10	11	12	13	13	16
$N_s^*(D_{cm})$	15	16	15	16	16	15	16	17	16	15

focus on a single polymer chain in solvent with varying sizes, where the polymerization degree of the polymer (N) is from 10 to 100 and the chain length of the solvent (N_s) changes from 1 to 80. When the solvent is small, $N_s = 1$, the system can be considered as a single polymer in normal size good solvents. The polymer chain is swollen in this region, and the static and dynamic properties of the single chain obtained in this work are in coincidence with Refs. [25,26]. When the solvent size N_s equals to the polymer size N , the system can be considered as in a melt of the same polymers. Thus the polymer chain should assume an ideal Gaussian state. When N_s is larger than the polymer size, this single polymer chain should collapse and shows the behavior of a short chain in large size solvents. As shown in Fig. 1, the mean square radii of gyration (Fig. 1a) and diffusion coefficients (Fig. 1b) of polymer chain are strongly affected by the solvent size. They decay fast with increasing solvent size, and then decrease very slowly after a critical solvent size N_s^* (listed in Table 1) which is obtained semiquantitatively via eyeballing. It seems that the decay of diffusion coefficients does not depend on the degree of polymerization of the polymer, since the polymer with different N possesses similar N_s^* (see Table 1). For $\langle R_g^2 \rangle$, the decay depends on both N_s and their N , i.e., the polymer with higher polymerization degree will have larger N_s^* . However, this critical solvent size N_s^* for $\langle R_g^2 \rangle$ of the polymer is a little bigger than $N^{1/2}$, which is expected by de Gennes [28]. We normalize the diffusion coefficients D_{cm} of the polymer in different chain-like solvents with that in the solvent with $N_s = 1$, and illustrate them in Fig. 1(c). It is shown that the decrease of the diffusion coefficients for the polymer is almost independent on N . It is implied that if we know the diffusion coefficients of certain polymer chains in normal solvent (i.e., the solvent with $N_s = 1$), the diffusion coefficients in varying size solvent can be estimated.

Here we introduce a tensor \mathbf{G} to describe the mass distribution of the polymer, whose elements have the following form [24]

$$G_{\alpha\beta} = \frac{1}{N} \sum_{i=1}^N (r_{\alpha i} - \bar{r}_\alpha)(r_{\beta i} - \bar{r}_\beta), \quad (7)$$

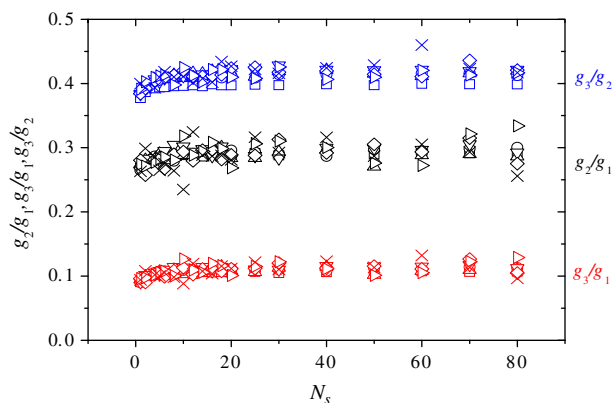


Fig. 2. (color online) The solvent size effect on the conformation of solute polymer chain with $N = 10(\square)$, $20(\circ)$, $30(\Delta)$, $40(\nabla)$, $50(\diamond)$, $70(\triangleright)$, $100(\times)$. g_1, g_2, g_3 are the three eigenvalues of tensor \mathbf{G} decrease in order, and black, red, blue symbols mean the ratios of g_2 and g_1 , g_3 and g_1 , g_3 and g_2 , respectively.

Table 2

The static scale exponent ν of single polymer in athermal solvent with varying sizes.

N_s	1	2	4	5	6	8	10
ν	0.594	0.573	0.555	0.552	0.550	0.546	0.548
N_s	12	14	16	18	20	25	30
ν	0.536	0.538	0.533	0.526	0.533	0.514	0.524
N_s	40	50	60	70	80		
ν	0.526	0.525	0.515	0.520	0.529		

where $\alpha, \beta = x, y, z$. $r_{\alpha i}, r_{\beta i}$ are the position vectors of the i -th monomer of α and β components, and $\bar{r}_\alpha, \bar{r}_\beta$ are the position vector of the mass center of polymer chain of α and β component, respectively. Sum of the three eigenvalues g_1, g_2, g_3 of \mathbf{G} are the mean square radius of gyration. If their ratios are equal to unity, the shape of the polymer is spherical. As shown in Fig. 2, the ratios $g_2/g_1, g_3/g_1, g_3/g_2$ increase with increasing N_s until the critical solvent size N_s^* is reached. Therefore, when $N_s < N_s^*$, the increasing solvent size makes the polymer tend to be thicker ellipsoids; when $N_s > N_s^*$, the thick ellipsoid shape of the polymer almost does not change with increasing N_s .

The static scaling exponent ν of the polymer in solvent with different sizes is obtained via the mean square radii of gyration of the polymer ($N = 10-100$), which is listed in Table 2 and shown in Fig. 3. In normal solvent, the static scaling exponent is $\nu = 0.594$, which is in agreement with $\nu = 3/5$ [28]. With increasing N_s , the static scaling exponent decreases from $\nu = 0.594$ for normal size solvent ($N_s = 1$) to $\nu = 0.526$ for large-size solvent ($N_s = 18$), and after that, the static scale exponent changes a little. That is to say, for small size solvent, increasing N_s makes the static scaling exponent ν of the polymer decrease, while for large-size solvent (the chain-like solvent), ν decreases a little with increasing N_s .

As is well known, Rouse model works well in polymer melts, while Zimm model is the best model of polymer dynamics in dilute solution, since Zimm model considers the hydrodynamic interaction, assuming that the chain drags the solvent in its pervaded volume with it, and treats the pervaded volume of the chain as a solid object moving through the surrounding solvent [29,30]. The dynamic structure factor is able to give more information about the dynamic behavior of polymer chain and can be used to predict the possible dynamic model for polymers. For $R_{reg}^{-1} \ll k \ll a^{-1}$ (a being a microscopic length scale of the order of a bond length) and the same period of time, the dynamic structure factor obeys the following relation [25,26]:

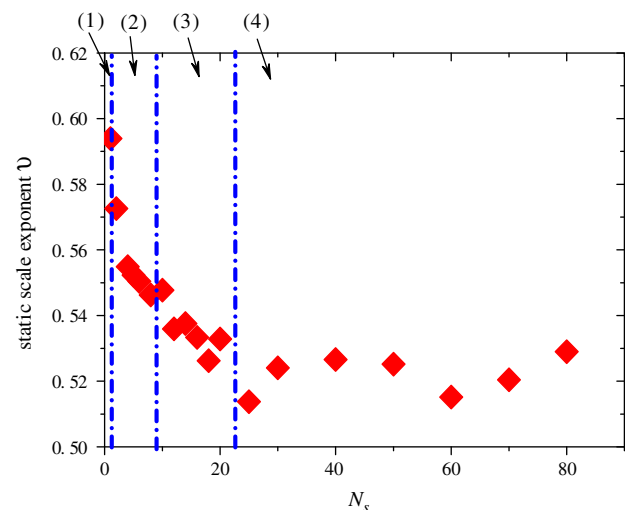


Fig. 3. (color online) Solvent size dependence of the static scale exponent ν of single solute polymer in different size solvent.

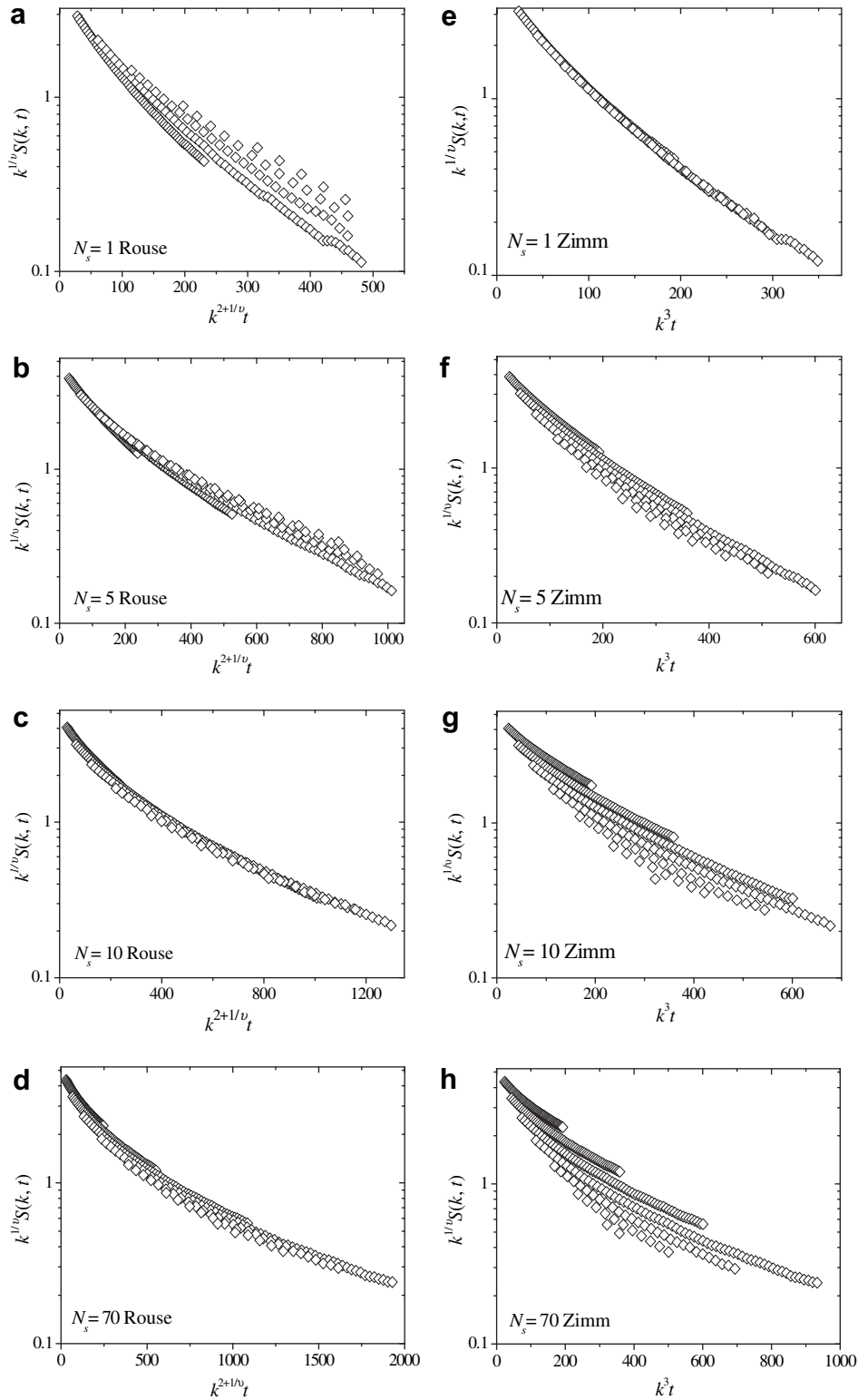


Fig. 4. The dynamic structure factors weighted by k^1 as a function of time t weighted by k^2 of single polymer chain ($N = 50$) in solvents with $N_s = 1$ (a, e), 5 (b, f), 10 (c, g), 70 (d, h), where $R_g^{-1} \ll k \ll a^{-1}$ (a being a microscopic length scale of the order of a bond length).

$$S(k, t) = k^{-1/\nu} f(k^z t) \text{ where } z = \begin{cases} 3.0 & \text{for Zimm model} \\ 2 + \frac{1}{\nu} & \text{for Rouse model} \end{cases} \quad (8)$$

Therefore, according to the dynamic structure factors of the polymers in our systems, four regions can be marked, as shown in

Fig. 3. The polymer dynamics can be described by Zimm model in region (1) ($N_s = 1$), deviates from Zimm model in region (2) ($1 < N_s < 8$), can be described by Rouse model in region (3) ($8 \leq N_s \leq 20$), and then deviates from Rouse model in region (4) ($N_s > 20$). Four typical dynamic structure factors of the polymer

with $N = 50$ in solvent with $N_s = 1$ (a, e), 5(b, f), 10(c, g) and 70(d, h) for regions (1), (2), (3) and (4) are given in Fig. 4, respectively. As is shown, the overlapped lines obtained in Fig. 4e and c illustrate that the single polymer with $N = 50$ behaves as Zimm model in solvent with $N_s = 1$ (i.e. region 1) and as Rouse model in solvent with $N_s = 10$ (i.e. region 3).

In order to illuminate the internal structure change of the polymers, the pair distribution functions $G(r)$ of the polymer with $N = 10$ –100 in solvent with $N_s = 1$ –80 are explored. Due to the similar solvent size dependence on $G(r)$ for the polymers with $N = 10$ –100, and for simplicity, we only show the pair distribution functions $G(r)$ of the polymer with $N = 50$ in solvent with $N_s = 1$ (a), 5(b), 10(c), 20(d) in Fig. 5. G_{PTRA} and G_{PS} represent the probability of a solute monomer contacting with the monomers of its own chain and the solvent beads respectively, and G_{SS} represents the probability of solvent beads contacting with solvent beads. It is seen that in normal solvent a solute monomer has more probability contacting with solvent beads than with the solute monomers of its own chain. With increasing N_s , G_{PS} decreases, G_{PTRA} increases, until they reach the critical solvent size N_s^* .

Furthermore, the solvent size dependence of the first peak G_0 of pair distribution function is obtained and shown in Fig. 5(e). It is shown that the total contact probability ($G_{\text{PTRA}} + G_{\text{PS}}$) of a solute monomer decreases and the solvent–solvent contact probability (G_{SS}) increases, which can be attributed to that the solvent with smaller sizes can penetrate into the polymers easily, while this penetration is difficult for larger solvents. Therefore, when $N_s < N_s^*$, increasing solvent size makes the solvent excluded from the polymer, and the polymer collapses. However, when $N_s > N_s^*$, the difficulty of penetration for these larger size solvent is similar, and the polymer cannot feel any difference among these larger size solvents, thus increasing solvent size does not make any further collapse of the polymer.

3.2. The properties of multi-chains in solvents with various sizes

The properties of multi-chains in varying size solvents are studied to explore the solvent size effect in concentrated polymer solutions. We are interested in whether the additional intermolecular interactions between polymer chains will change this

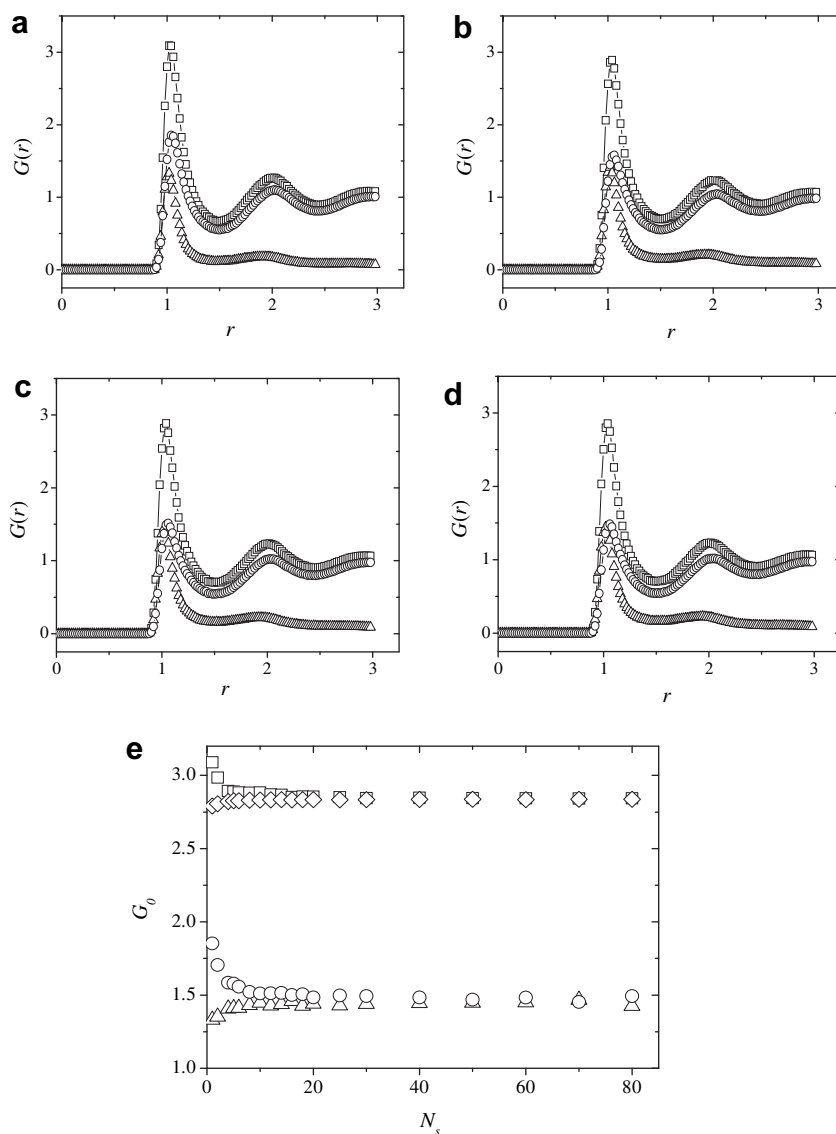


Fig. 5. Solvent size dependence of the pair distribution function of single polymer chains ($N = 50$) in solvents with $N_s = 1$ (a), 5(b), 10(c), 20(d) and the value of the first peak of pair distribution function (e), where G_{PTRA} (Δ), G_{PS} (\circ), $G_{\text{PTRA}} + G_{\text{PS}}$ (\square), and G_{SS} (\diamond) are given respectively.

solvent size effect. We firstly investigate concentrated systems with $\phi = 0.22$ ($\phi = N_p/N_{tot}$ being the volume fraction of the solute polymers, where N_p is the total number of monomers of the polymers) and four polymer chain lengths $N = 20$ ($n_p = 102$), 30 ($n_p = 68$), 60 ($n_p = 34$), 80 ($n_p = 26$), where n_p is the number of solute polymer chains. For each polymer solutions, the solvent size ranges from $N_s = 1-80$. The mean square radii of gyration and diffusion coefficients of mass center of the polymers in these concentrated systems show similar decay behaviors as those of single polymer solutions, and similar critical solvent sizes N_s^* are found (as shown in Fig. 6). The first peak G_0 of the pair distribution functions of these polymers are shown in Fig. 7. With increasing solvent size, contact probabilities (G_{PTRA} , G_{PS} , G_{SS}) show similar behavior as those of single polymer chain in different solvents. Moreover, the solvent size dependence of the inter-molecular contact probability (G_{PTER}) of the polymers is similar as that of G_{PTRA} . The increase of solvent size makes the polymers have more probabilities contacting with other solute polymers and less probabilities contacting with solvents, which makes the difference among these three contact probabilities (G_{PTRA} , G_{PTER} , G_{PS}) obvious. Monomers of the polymers with larger N have more probabilities contacting with their own chain monomers, and less probability contacting with monomers of other solute polymers or solvent molecules. Therefore, the solvent size effect on the properties of the polymers in concentrated system is similar as that in single polymer dilute solutions.

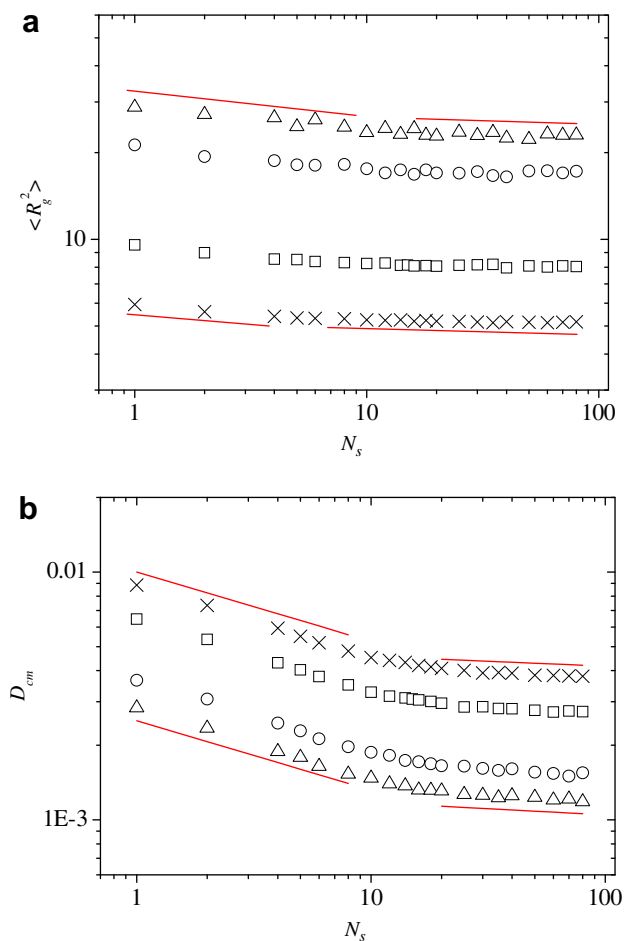


Fig. 6. (color online) The solvent size dependence of mean square radii of gyration (a) and diffusion coefficients (b) of polymer chains with $N = 20$ (x), 30 (□), 60 (○), 80 (Δ) in various size solvent with $\phi = 0.22$. The corresponding lines are drawn for visual guide.

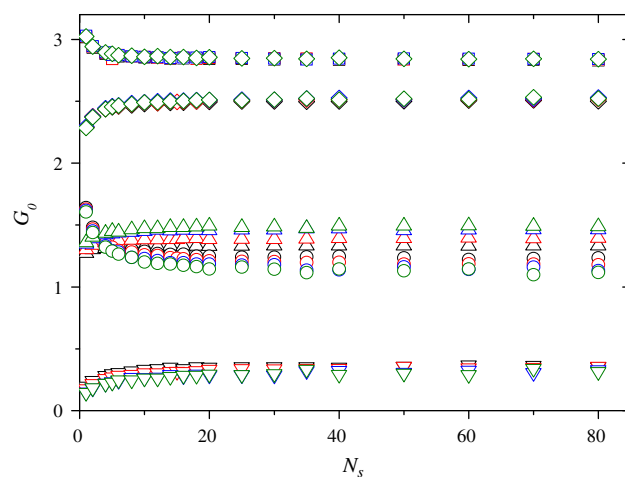


Fig. 7. (color) Solvent size dependence of the first peak of pair distribution function of solute polymers with $N = 20$ (black), 30 (red), 60 (blue), 80 (olive) in concentrated solution ($\phi = 0.22$). Symbols (□, Δ, ○, ◇) have the same meaning as aforementioned and symbol (▽) represents G_{PTER} .

The solvent size dependence of $\langle R_g^2 \rangle$ and D_{cm} of the polymers with $N = 30$ in three concentrated solutions $\phi = 0.22$ ($n_p = 68$), 0.50 ($n_p = 155$), 0.80 ($n_p = 247$) are given in Fig. 8. Both properties in these concentrated polymer solutions show similar attenuation

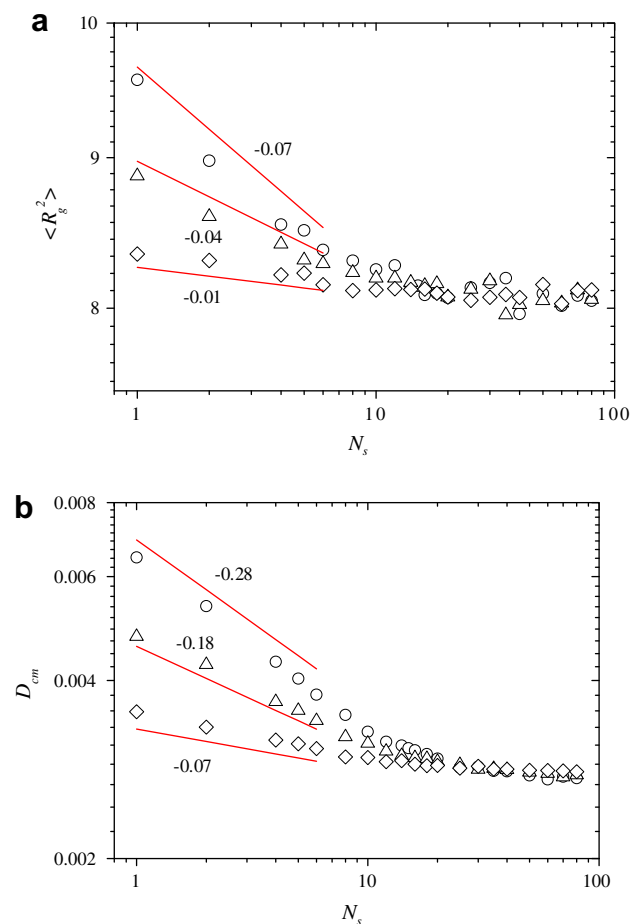


Fig. 8. (color online) The solvent size dependence of mean square radii of gyration (a) and diffusion coefficients (b) of polymer chains with fixed $N = 30$ and the volume fraction is $\phi = 0.22$ (○), $\phi = 0.50$ (Δ), $\phi = 0.80$ (◇). The lines are drawn for visual guide, and the numbers above those lines are the corresponding scales.

behaviors as those in single polymer solutions, and similar critical solvent sizes N_s^* are observed. Besides, with increasing N_s , $\langle R_g^2 \rangle$ (Fig. 8a) and D_{cm} (Fig. 8b) of the polymers in lower concentration systems decay faster than those in higher concentration systems. Furthermore, the asymptotes of $\langle R_g^2 \rangle$ and D_{cm} of the polymer are dominated by the chain length of polymers, which implies that the diffusion behavior and mean square radius of gyration of the polymers can be predicted for a given polymer solutions with different concentrations when the solvent size is higher than N_s^* .

4. Summary

The static and dynamic properties of polymers in solvents are strongly affected by the solvent size. Both the mean square radius of gyration and diffusion coefficient of polymers decay fast with the increase of chain length of solvent N_s , until a critical solvent size N_s^* is reached. Moreover, for diffusion coefficient, this decay seems only to depend on the solvent size, while for the radius of gyration of polymers, this decay depends on both the solvent size and the length of polymers. Moreover, the increasing solvent size makes solute polymer tend to be thicker ellipsoid and have more probability contacting with solute chains than solvent beads until reaching their critical solvent sizes. After N_s^* , the shape of polymer is relatively insensitive to the increasing N_s . These behaviors are also found in concentrated polymer solutions. The above results may help us to understand the physical essence of polymer solutions.

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